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ELASTIC PROPERTIES RESEARCH

Seventh Progress Report

October 1, 1962 - March 31, 1963

Contract No. AF 33(616)-6789

prepared by

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and

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DEPARTMENT OF MATERIALS SCIENCE

STANFORD UNIVERSITY • STANFORD, CALIFORNIA

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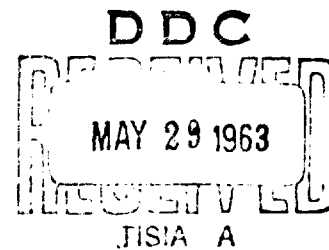
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I. INFLUENCE OF ELASTIC MODULI ON MECHANICAL PROPERTY AND ATOMIC MOBILITY CHARACTERISTICS OF CRYSTALLINE SOLIDS AT ELEVATED TEMPERATURE   (O. D. Sherby)

Very little is yet known about the influence of temperature on the elastic properties of single and polycrystalline solids, especially above one-half the absolute melting temperature. Much more experimental and theoretical work is necessary. At the A.R.L. annual contractors' meeting in February, 1963 we attempted to show, in the short time allotted us, some of the important contributions of elastic properties to other elevated temperature properties of crystalline solids. This is reviewed briefly in the following sections.

(1) <u>Plastic properties of polycrystalline solids</u>. Research on the creep of polycrystalline metals[1] has revealed three important factors that contribute to the strength of such solids: (1) diffusion rate of atoms, (2) grain size and (3) elastic modulus of the material. It has been shown that the strength of a polycrystalline metal above half the absolute temperature can be predicted by the relation

$$\sigma = 1.7 \cdot 10^{-6} \, \dot{\epsilon}^{\frac{1}{5}} \, \frac{E}{D^{1/5} L^{2/5}} \quad , \tag{1}$$

where σ is the ultimate tensile strength in psi (or flow stress since strain hardening is negligible at elevated temperature), D is the diffusion coefficient (in cm^2/sec), L is the grain diameter (in cm), $\dot{\epsilon}$ is the strain rate (in secs.$^{-1}$), E is the average elastic modulus (in psi) and the constant has units of $cm^{-4/5}$. Thus, if one were to compare all metals of comparable grain size and at a temperature where the diffusion coefficient was the same, the strength (at a given strain rate) will be proportional to the average elastic modulus. This is shown to be the case in

Fig. 1 for a number of metals.

The importance of elastic modulus also comes into play in the calculation of activation energies for creep. For example, it has been shown that the activation energy for creep is normally higher than that for self-diffusion at temperatures above half the absolute melting temperature[2-4]. This is because the modulus of a material partly controls the creep rate, probably through its influence on the height a dislocation must climb before it surmounts a barrier[5]. Since E changes with temperature it will influence the creep rate above and beyond the influence of the change of the diffusion coefficient with temperature. If the activation energy for creep is determined at constant $\frac{\sigma}{E}$ rather than at constant σ (the usual way) an activation energy for creep is then obtained equal to that for self-diffusion. Examples of this consideration on determination of activation energies for creep is given in Section IV of this progress report.

(2) <u>Volume self-diffusion in crystalline metals</u>. Zener has derived a theoretical expression for D_o, the pre-exponential term in the diffusion coefficient[6]. In the derived expression the temperature coefficient of the elastic modulus is introduced as a factor that controls the entropy of activation of the diffusion process. The expression for D_o as given by Zener is

$$D_o = \gamma a^2 \nu e^{\Delta S/R} \qquad (2)$$

where γ is a coefficient related to the geometry of atomic jumps, a is the jump distance, ν is the frequency of vibration of atoms, ΔS is the entropy of activation and R is the gas constant. The entropy of activation is given by
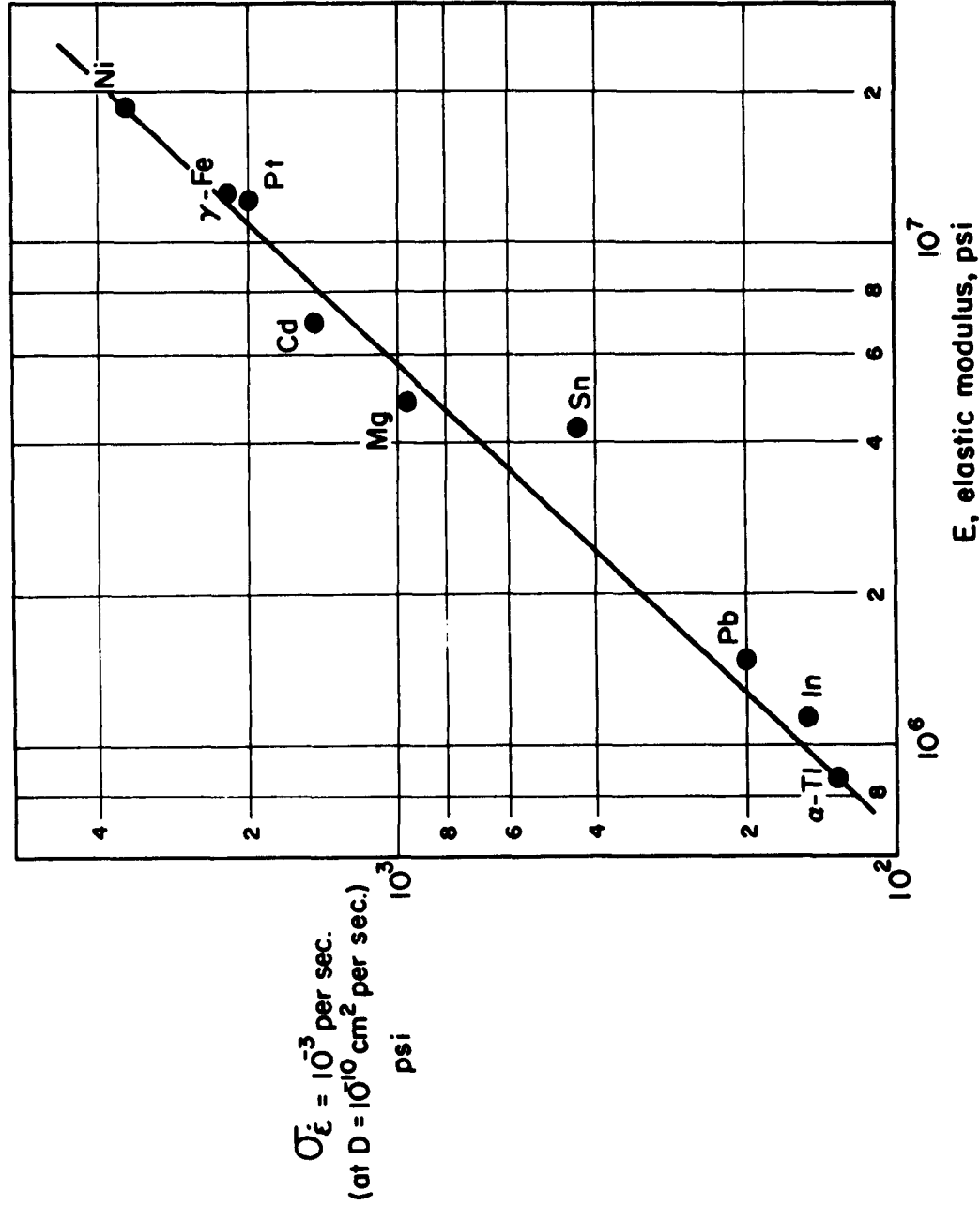
Fig. 1   Influence of elastic modulus on the elevated temperature
         strength of various metals (data taken from reference
         (1)). Comparison made with metals of comparable
         grain size (L≈.05 cm) and at same value of diffusion
         coefficient (D=10^{10} cm²/sec.).

$$\Delta s = \lambda \beta \frac{Q}{T_m} ,\qquad\qquad (3)$$

where λ is a numerical coefficient about equal to one, Q is the activation energy for self-diffusion, T_m is the absolute melting temperature and β is the temperature coefficient of the elastic modulus given by

$$\beta = - \frac{d(E/E_o)}{d(T/T_m)} . \qquad\qquad (4)$$

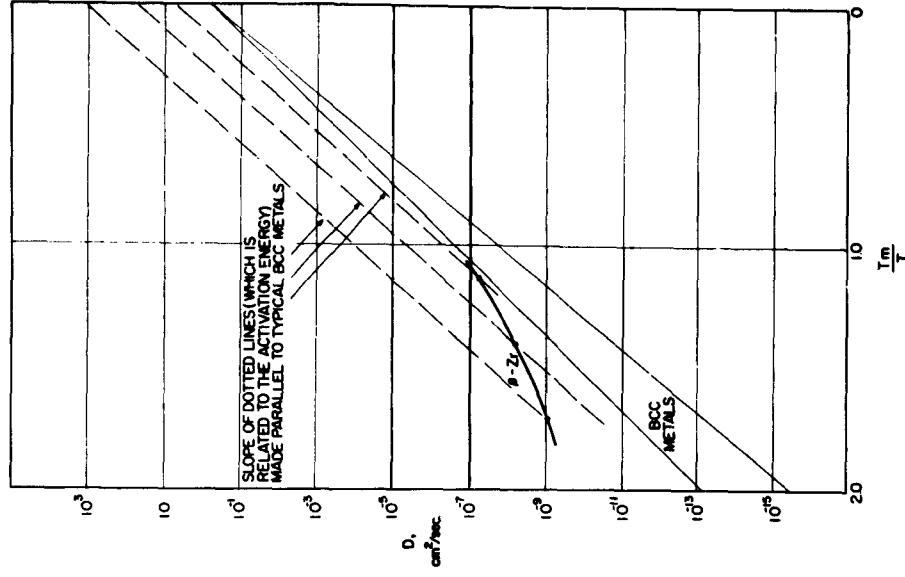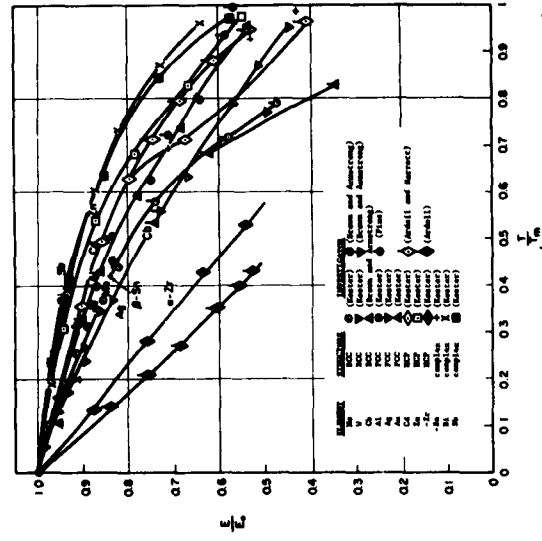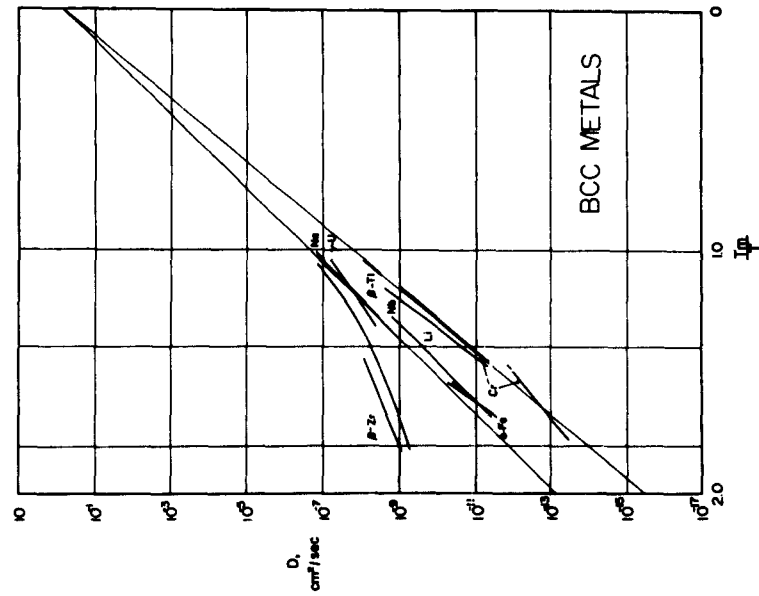In this expression E is the modulus at temperature T and E_o is the modulus at absolute zero.

Since the constants, γ , a, ν and $\dfrac{Q}{T_m}$ are about the same for most metals* it can be readily seen that D_o should be proportional to β . That Zener might be essentially right in his theoretical analysis is evidenced by the fact that β is about the same for many metals and similarly D_o is

---

* γ is related to the geometry of atomic jumps and Zener has indicated that this should be unity for the case of an atom-vacancy exchange process.   a, the jump distant, would be approximately equal to the lattice parameter, about 2 Å for most metals. ν , the frequency of atomic vibration, is generally taken as 10^{13} per second; a vigorous approach to the determination of this characteristic of atoms[7], however, suggests that it is proportional to the square root of $\dfrac{Ea}{m}$ where E is the elastic modulus, a is the lattice spacing and m is the atomic mass. The data in Fig. 5 on experimental D_o values for liquid and solid self-diffusion, in fact, do reveal a trend between D_o and the atomic mass suggesting that the relation $\nu = \dfrac{1}{2\pi}\sqrt{\dfrac{Ea}{m}}$ may be essentially correct. The importance of the modulus term E in the above equality has not been evaluated; in Eyring's expression[8] for ν , the atomic mass is introduced in a similar way but a modulus term is absent. $\dfrac{Q}{T_m}$ is about constant for a given crystal structure since it has been shown[9] that $Q = R T_m (k_o + V)$ where k_o is a crystal structure factor (14 for BCC metals, 16 for HCP metals, 17 for FCC metals and 21 for diamond structure) and V is the valence. Since k_o is much greater than V, $\dfrac{Q}{T_m} \simeq R k_o$.

about the same for these same metals ($D_o \simeq 1$ cm^2 per second). In the case of zirconium where anomalously high diffusion rates are obtained the behavior can be associated with an exceptionally large value of β. This peculiar diffusion behavior of beta zirconium (which is body-centered-cubic) is compared with other pure metals in Fig. 2 where the diffusion coefficient is plotted as a function of the reciprocal homologous temperature $\frac{T_m}{T}$. The elastic constants for a number of metals are plotted in Fig. 3. As can be seen, the value of β for zirconium (only alpha zirconium is plotted since data for beta zirconium is not yet available) deviates considerably from the other metals. If the activation energy for self-diffusion of beta zirconium is assumed to be about normal then the diffusion data (Fig. 2) for this material can be interpreted as follows: the D_o is unusually high for this metal and furthermore D_o varies with temperature, decreasing with increasing temperature. This suggested variation is illustrated in Fig. 4. High values of D_o are in harmony with the high value of β for zirconium.

Another example of the possible influence of elastic properties on solid state diffusion can be given. It has been shown that ferromagnetism influences the self-diffusion rate of iron[10, 11] and that when the Curie temperature is approached the atomic mobility is increased more rapidly than a linear increase of log D versus (1/T) predicts. A similar change in the elastic properties of iron has also been observed[3, 4]; that is, the modulus drops much more rapidly than linearly with increase in temperature in the vicinity of the Curie temperature. Borg[12] has successfully related the changes in self-diffusivity with temperature as ferromagnetism is lost with

Fig. 4 Comparison of the self-diffusion of beta zir-
conium with other BCC metals illustrating the
proposed variation of D_o with temperature.

Fig. 3 Normalized Young's moduli as a function of
homologous temperature, T/T_m, for twelve
pure polycrystalline metals. Note anomalous
behavior of α-zirconium.

Fig 2   Rate of self-diffusion for BCC metals
plotted as logarithm D versus $\frac{Tm}{T}$

the Zener relation on the assumption that D_o is increased with increase in the coefficient β of equation (3).

As encouraging as these results may be in support of Zener's theory there are two difficulties which must be overcome before a clearer understanding of the influence of elastic constants on atomic mobility is evolved. These are discussed in the following sections.

Absolute values of D_o in Zener expression. A major discrepancy in the correlation between Zener's theory of D_o and experiment is observed when the absolute values of D_o as obtained from equation (2) are compared with experimental values[13]. In fact, as can be seen in Fig. 5, the theoretical values are generally about 10^2 larger than the actual values (with considerable scatter). This discrepancy is true both for solid state diffusion as well as for liquid state diffusion. These results suggest that an important contributing factor to D_o may have been overlooked by Zener.

Method of obtaining β. Zener obtained β values by determining the slopes of the E/E_o versus T/T_m curves at low temperatures, below $0.5\ T_m$. He purposely avoided using high temperature modulus information because these data typically show curved relations rather than linear ones. Zener attributed such curvatures to the contribution of grain boundary relaxation to the observed modulus. It is undoubtedly true that some of the reported elevated temperature data on modulus of pure metals is complicated by such boundary relaxation. In many cases, however, a curvature is observed even in the case of single crystals. An example of such behavior is given for zinc single crystals in Fig. 6; the modulus curve for polycrystalline zinc is shown on the same graph. As can be readily seen the single crystal and polycrystal data all reveal a similar temperature dependence. Work by

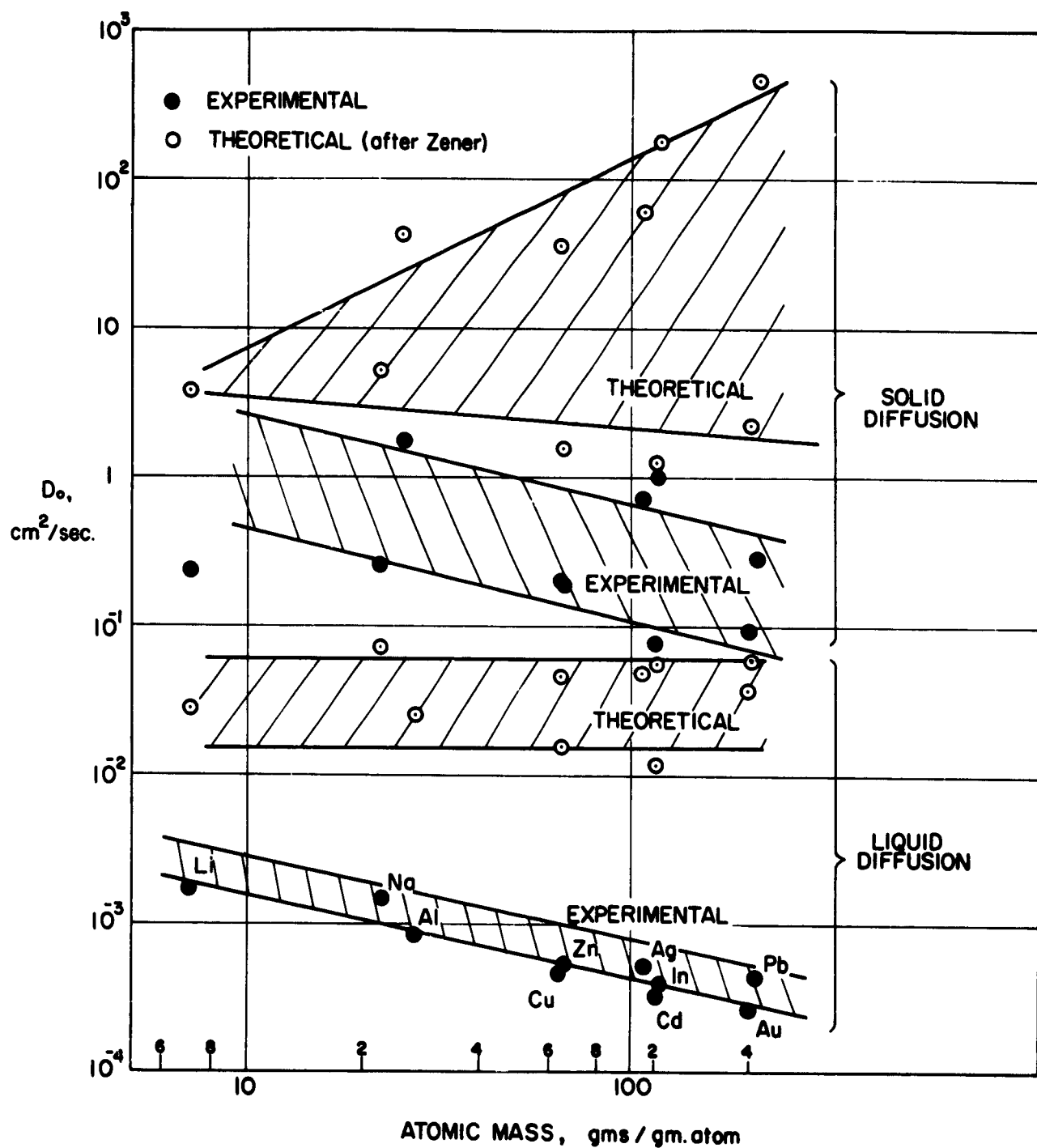Fig. 5 Comparison of experimentally obtained D_o values for liquid and solid self-diffusion in metals with D_o values as predicted by Zener.
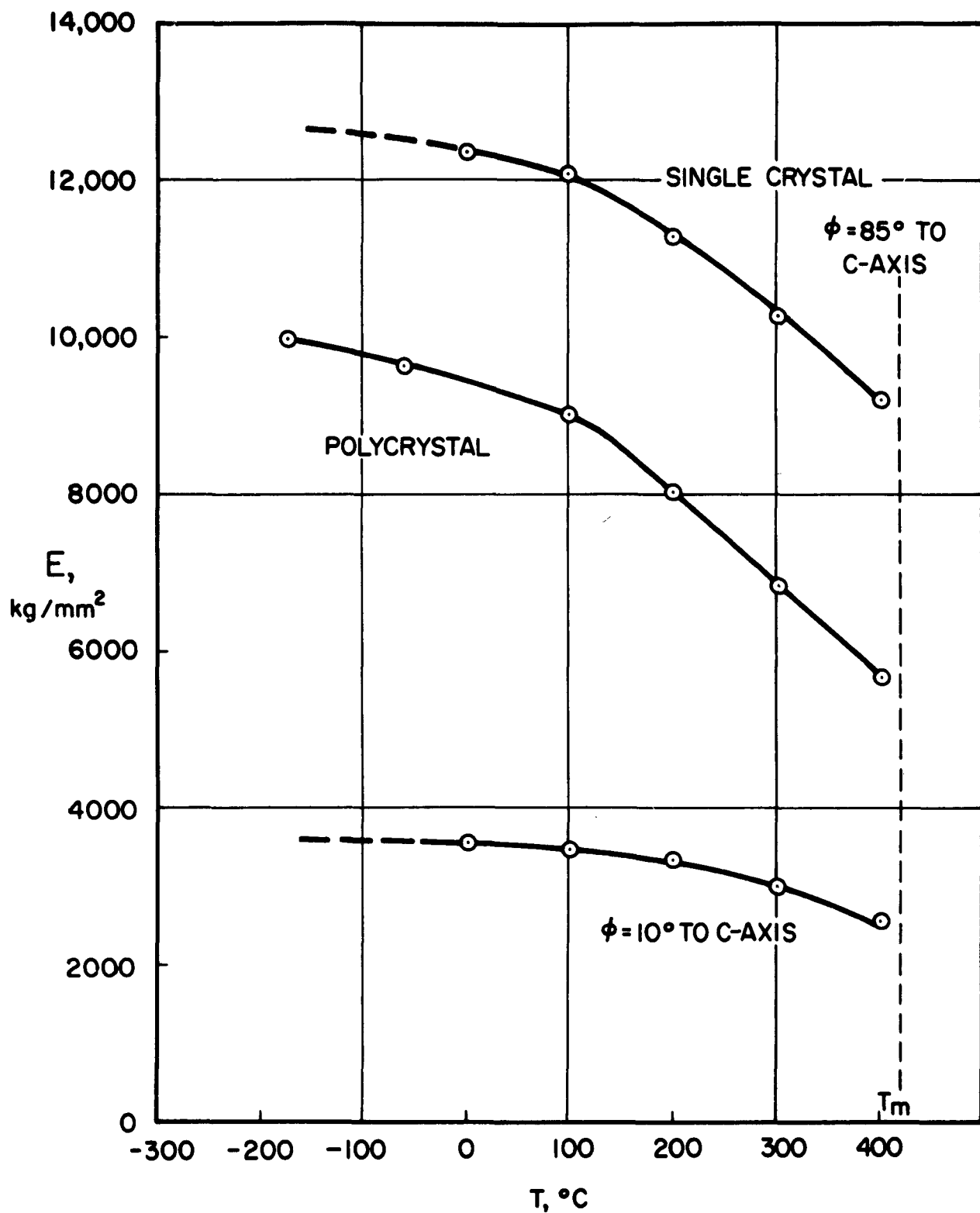
FIG. 6   Dynamic moduli of elasticity of single crystalline and polycrystalline zinc as a function of temperature. ϕ is the angle between the c-axis and the specimen axis.   Single crystal data after Reinacher and Scheil[18] polycrystal data after Koster[16]

Brown and Armstrong[17] on the elastic properties of single crystals of W and Mo revealed similar curves.

Obviously if such curvatures in the elastic properties above 0.5 T_m reflect the true behavior of the material with respect to the bonding characteristics of the crystal lattice, it is this type of data that is needed to correlate with the corresponding diffusion data (since almost all diffusion studies have been performed much above 0.5 T_m). Such analyses have not been attempted to date simply because very few determinations of elastic constants of single crystals have been performed above 0.5 T_m; on the other hand, reliable diffusion data are now available for 23 different metals[9].

If β in Zener's entropy expression (equation 3) changes with temperature it might be expected that logarithm D should be a non-linear function of 1/T. Curvature in such plots has already been illustrated for zirconium in Fig. 2. That other diffusion data might exhibit some curvature has been suggested by several investigators[14, 19].

II. INFLUENCE OF GRAIN BOUNDARY RELAXATION ON THE ELASTIC PROPERTIES OF POLYCRYSTALLINE AGGREGATES   (A. J. Ardell)

The mathematical treatment in the previous progress reports has been developed for the purpose of providing greater insight into the atomic mechanism of grain boundary relaxation; this, in turn, would increase our knowledge of the nature of internal boundaries in metals. It is indeed a pity that the experimental phenomenon of anelasticity, which has proved so fruitful for investigating interactions between substitutional and interstitial foreign atoms with the metallic lattice, has led to nothing conclusive about grain boundaries. This is partly because grain boundary relaxation is an inhomogeneous process in the sense that it occurs in inhomogeneous regions

throughout a given specimen, and partly because existing data have been mis-interpreted by failure to account for the distribution of relaxation times involved, despite the fact that the existence of this distribution has long been recognized[20, 21]. These two aspects will be discussed in more detail shortly. Suffice it to say now that the consequences of the inhomogeneous nature of grain boundary relaxation impose certain limitations on the mathematics.

In the sixth progress report[22] it was stated that the distribution of relaxation times is more likely due to a distribution of facet sizes than grain diameters. It was also speculated that the former distribution would be broader than the latter. To investigate this possibility a photomicrograph of annealed pure aluminum was taken and enlarged to facilitate facet size measurement. The resulting histogram with fitted curve is shown in Fig. 7. The fitted curve is replotted on a logarithmic scale in Fig. 8 (in both figures the facet size scale is arbitrary). As is evident from Fig. 8 the distribution in facet length L is not lognormal, though for comparison it is possible to extract a half-width, the value of which is 0.996. This is roughly 2-1/2 times the lognormal β's for grain diameters of Al and Sn reported by Feltham[23]. The half-width value of 0.996 is still far too small to account for the observed breadth of internal friction due to grain boundary relaxation in aluminum, which requires a β of 4.28[22]. According to McLean[24] copper and silver require comparable β's, so that we may tentatively regard half-width values of 3-1/2 to 4-1/2 as typical. An assumed proportionality between τ_o and L^2 offers no significant improvement in fit.

Lack of lognormality in the facet size distribution can be interpreted as proof that the facet size, not the grain size, is the important parameter
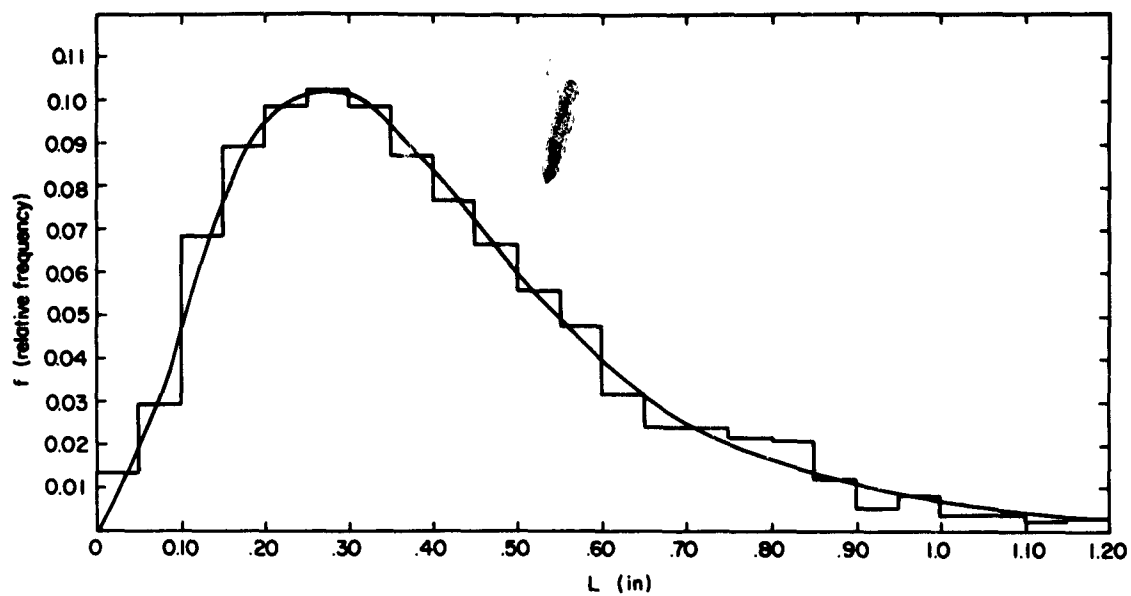
Fig.7 Histogram of relative frequency vs. grain edge length for pure annealed aluminum with continuous fitted curve.
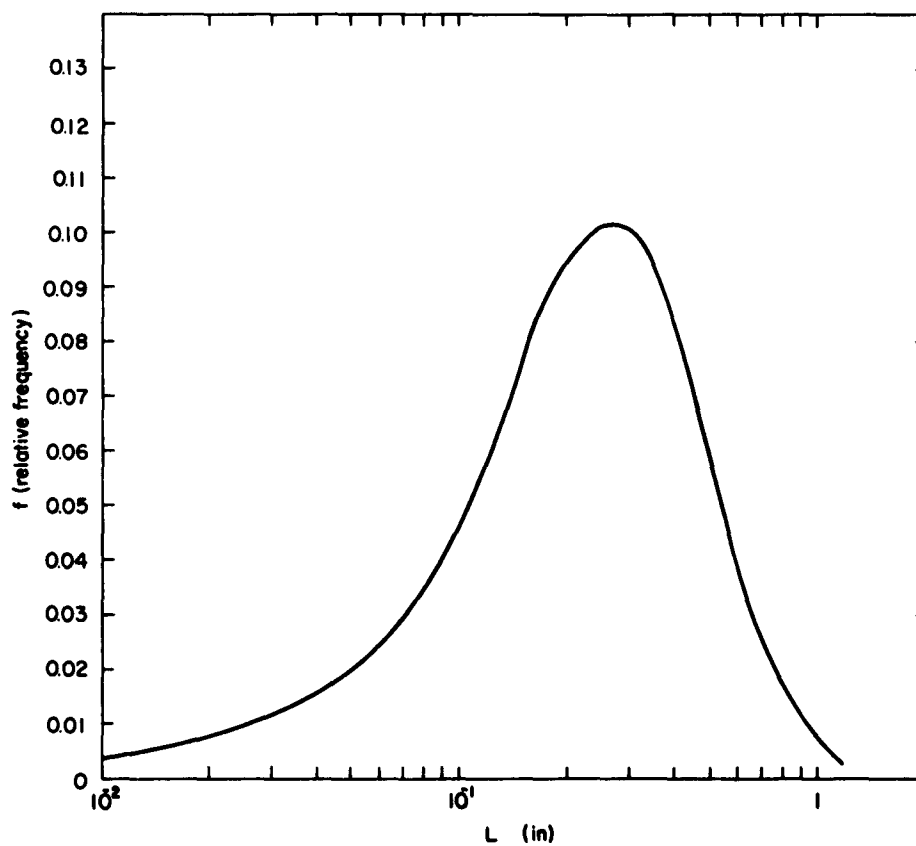

Fig. 8 Relative frequency vs. the logarithm of grain edge length for pure annealed aluminum.

in the quantity $(\nu Le^{H/RT})$. Letting D represent grain size, a lognormal distribution of grain size means a symmetrical distribution in $\ln(D)$. More specifically, if $\bar{D}$ is the mean grain size, the distribution of $x = \ln(D/\bar{D})$ is symmetrical about $x = 0$ if the distribution of x is lognormal. Similarly, the distribution of $y = \ln(L/\bar{L})$ is symmetrical about $y = 0$ if the distribution of y is lognormal. If we assume τ_o proportional to L, it is easy to show that

$$y = -(H/R)(\xi - \bar{\xi}) \ . \tag{5}$$

Therefore, if the distribution of y is lognormal, the distribution of ξ is symmetrical about $\xi = \bar{\xi}$, and the resulting curve of J_2/J_u is symmetrical about its maximum. This is illustrated in Fig. 1 of the sixth progress report[22]. It can also be seen from this figure that the experimental curve is not symmetrical about its maximum, but is skewed to high values of $1/T$, or equivalently, to high values of ξ. On the other hand, Fig. 8 of this report reveals that $f(y)$ is skewed to the left which, through equation (6) predicts that $g(\xi)$ should be skewed to the right. Since grain size distributions are lognormal[23] they should yield symmetrical curves of J_2/J_u. Since this is not the case we may conclude that the facet size distribution is the governing one as would be expected.

It remains to investigate possible reasons for the lack of fit between experimental and theoretical curves. One may immediately inquire into the effect of grain boundary misorientation. Low-angle boundaries which can be successfully described by dislocation models are difficult to shear, whereas high-angle boundaries will shear in a viscous manner at low stresses. We may anticipate that the activation energy associated with viscous-like

motion of high-angle boundaries depends on the structure of the boundary, although it is difficult to envisage how the structure changes with misorientation angle. One might expect that the activation energy is a sensitive function of misorientation angle in the region of transition between low-angle and high-angle, but that it is relatively insensitive in the high-angle region. This, however, is contradicted by the theoretical calculations of Li[25]. By assuming that shear motion of high-angle tilt boundaries occurs by the mechanism of grain-boundary jog propagation, he derives an expression for the activation energy of grain boundary shearing as a function of misorientation angle which indicates a rapid variation of activation energy with angle. The indications are, however, that Li's equation is more applicable to shearing behavior at stress levels considerably higher than those normally encountered in grain boundary relaxation experiments. It is known that at stress levels sufficient for plastic deformation in a material, grain boundaries no longer deform in a viscous manner[26]. In any event, a distribution in activation energy will result in a change in the width of grain boundary relaxation curves with temperature (or frequency), and although the temperature ranges in the literature are small, the accuracy with which activation energies are determined indicate no large changes in peak width. From this we may conclude tentatively that the contribution of a distribution of activation energies is small.

Let us now examine the consequences of the heterogeneous nature of grain boundary relaxation. In any given specimen the grain boundaries will experience varying initial shear stress depending upon the angle between the boundary normal and the applied stress. Consider the idealized case of cubical grains of the same size in a specimen subject to uniform tension.

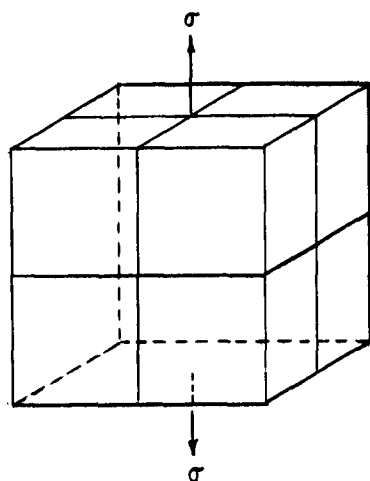Two important points are illustrated in Figs. 9a and 9b.
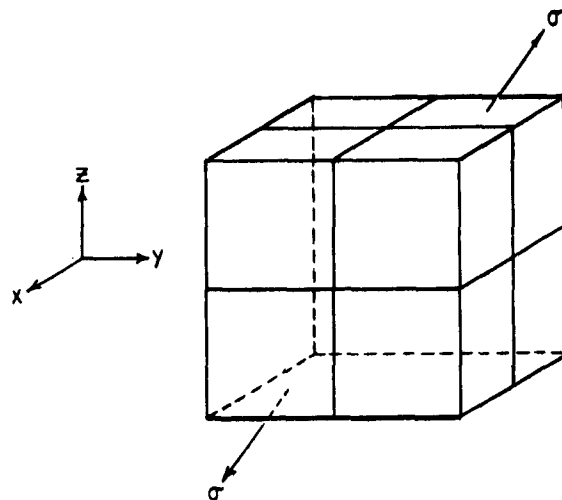
Figure 9a   Figure 9b

In Fig. 9a there is no shear stress acting in any of the boundaries so that the material is unrelaxed at all times, i. e., it behaves as if it had an infinite relaxation time. Thus we see that even though there is an intrinsic single relaxation time associated with the specimen, the stress state is such that no relaxation can occur. Reference to Fig. 9b reveals that unless σ acts along a cube diagonal, the initial shear stress differs for boundaries with normals in the x, y, and z directions. In this way it is possible for a specimen with a single intrinsic relaxation time to behave as if it had as many as three relaxation times.

The implication of this example is an important one; it is possible that the extreme breadth of grain boundary relaxation curves is due largely to the way the applied stress is initially distributed on boundaries, thus indicating that an exact fit between theory and experiment would yield more

information about the stress distribution on the grain boundaries than the nature and properties of the boundaries themselves. It is suggested, therefore, that before any future attempts are made to fit experimental grain boundary relaxation curves, experiments be carried out with the following improvements:

1. Data should be obtained well into the region where the characteristic background internal friction is dominant so that the internal friction due to grain boundary relaxation can be separated unambiguously from the background. The average relaxation time may then be identified with the maximum in the curve of $(Q^{-1}xM_u/M)$.

2. Measurement of the average facet size should be made so that the dependence of Q^{-1} and M/M_u on this parameter can be established.

3. Experiments should be conducted over wide enough frequency ranges to determine whether there is a significant contribution due to an activation energy distribution. Such a contribution will manifest itself in a change of the width of Q^{-1} curves at the different frequencies.

4. Care should be taken to insure that preferred orientation is absent in test specimens so that there is a preponderance of high-angle boundaries.

It is planned to write a paper summarizing the various factors influencing grain boundary relaxation discussed during this program.

III. INFLUENCE OF SOLID SOLUTION ALLOYING ON THE ELEVATED TEMPERATURE ELASTIC AND PLASTIC PROPERTIES OF POLYCRYSTALLINE SOLIDS
(H. Ledbetter)

It is proposed to investigate the high temperature mechanical behavior of various solid solution alloys in the Cu-Zn system. Although the creep characteristics of pure metals are fairly well understood (see reference (1) for example), only preliminary studies have been made toward an understanding of creep in solid solutions. Important work in this area has been done by Weertman[27-30] as well as by Sellars and Quarrell[31].

Weertman[27, 28] has given the most detailed and quantitative mechanistic theories of creep, both for pure metals and for solid solutions. At intermediate stresses his results for the steady state creep rate show a power law type stress dependence and an exponential temperature dependence of the form

$$\dot{\epsilon} = K \frac{\sigma^n}{kT} \exp \ (-Q/RT) \tag{6}$$

where n is 4.5, 3.0, or 2.5 depending on whether the rate controlling process is dislocation climb, solute drag on moving dislocations (micro-creep), or motion over Peierls hills respectively. For the first case the creep rate can be written more explicitly as

$$\dot{\epsilon} = K' \ \frac{D\sigma^{4.5}}{M^{0.5} E^{3.5}} \tag{7}$$

which shows the strong dependence of the steady-state creep rate on the diffusivity D, the elastic modulus E, and the density of active F-R sources M.

An earlier theory of Weertman's[5], which required the production

of immobile dislocations, gave the result

$$\dot{\epsilon} = K'' \frac{D\sigma^4 LL'M}{E^3} \tag{8}$$

where L and L' are interpreted as the grain size and sub-grain size.

When microcreep controls, Weertman[28] has given for low stresses a general expression for the creep rate due to viscous dislocation glide

$$\dot{\epsilon} = 0.35 \frac{\sigma^3}{AE^2} \tag{9}$$

where A depends upon the particular rate controlling mechanism (Cottrell locking, Suzuki locking or Fisher locking) and is a function of the diffusivity.

Comparison of Weertman's theories with experiment has been encouraging indeed, though only qualitative. Equation (7) should apply to pure metals while equation (9) should apply to solid solutions. Alloying should reduce the stress exponent from 4.5 to 3.0. Ni[29] and Al[31] both have shown a 4.6 stress exponent at low stresses, giving close agreement with the theory. Further, Weertman's theoretical calculations are in reasonable agreement with the semi-empirical equation given by Sherby[1] for the steady state creep rate in pure metals

$$\dot{\epsilon} = 10^{29} L^2 D \left(\frac{\sigma}{E}\right)^5 \tag{10}$$

which again emphasizes the importance of the grain diameter L, the diffusivity D, and the elastic modulus E in high temperature creep.

For alloys there is also good agreement between theory and experiment. Various alloys of In and Pb have been shown by Weertman[30] to have

the predicted reduction in the stress exponent upon alloying. Aluminum alloys show a similar effect[31]. But in all of these cases, both diffusion and elastic constant data were not available so that a quantitative comparison between experiment and theory was not possible.

Sellars and Quarrell[31] have investigated the high-temperature mechanical behavior of alloys in the Au-Ni system (which exhibits continuous solid solubility). Using constant stress compression tests they found a power law of 5.6 for the pure metals and a power law of 3.0 to 3.5 for the alloys. A strong dependence upon diffusivity was also demonstrated. However, lack of elastic constant data prevented a precise comparison with Weertman's theory.

To date, no detailed investigation of creep in solid solutions has been made carefully considering the combined effects of changes in diffusivity, elastic modulus and grain size. In fact, no binary system seems to exist where both the diffusivity and the elastic constants are accurately and completely known. Such an investigation is the purpose of the present work. The Cu-Zn system seems the best choice because of the availability of complete and precise diffusion data[32-36], and the partial availability of elastic constants[37], in addition to some perhaps useful electronic correlations. Alloys of interest include: 0, 10, 20, 30 atomic percent Zn (in the fcc or α phase); 50 atomic percent Zn (in the BCC or β phase); and 65 percent Zn (in the complex cubic or γ phase). Constant stress compression creep tests will be conducted in the range 550 to 700° C, using 4 mm diameter specimens and stresses up to about 1000 psi. This represents an homologous temperature range above 0.5 T_m for all the

alloys. Grain size will be controlled to about 0.5 mm. Additional elastic constants will be determined by measuring the dynamic modulus at temperature using resonance techniques in specimens of fixed geometries. Work in progress includes grain size control and the construction of a constant stress compression creep apparatus fitted for inert atmosphere testing.

IV. INFLUENCE OF MODULUS ON THE TEMPERATURE DEPENDENCE OF THE ACTIVATION ENERGY FOR CREEP AT HIGH TEMPERATURES (A. J. Ardell and C. R. Barrett)

It has been established experimentally[1] and theoretically[5, 27, 38] that high temperature creep of polycrystalline pure metals is a thermally activated process and may be represented by the general expression:

$$\dot{\epsilon}_s = A \; f(\sigma, T) \; D \tag{11}$$

where $\dot{\epsilon}_s$ is the steady state creep rate, A is a constant depending on the internal structure of the material, f is some function of the applied stress, σ, and test temperature, T, and D is the self-diffusion coefficient. If we separate D into its temperature dependent and independent portions, then it is possible to rewrite equation (11) as

$$\dot{\epsilon}_s = A' \; f(\sigma, T) e^{-Q_{sd}/RT} \tag{12}$$

where Q_{sd} is the activation energy for self-diffusion. Assuming a simple Arrhenius type relationship between creep rate and temperature at a given constant stress, the apparent activation energy for creep, Q_c, can be given by the expression

$$Q_c = \frac{-R \; d \; \ln \dot{\epsilon}_s}{d \; (1/T)} \quad . \tag{13}$$

It is obvious that if $f(\sigma, T)$ is not a function of temperature, then $Q_c = Q_{sd}$.

Sherby[1] has shown that the steady state creep rate for pure metals can be represented by

$$\dot{\epsilon}_s = SL^2 D \, (\sigma/E)^n \qquad (14)$$

where S is a constant, L is the grain diameter, and E is the average (un-relaxed) elastic modulus, and n is a constant equal to 5 over a wide range of stress. The apparent activation energy for creep calculated from this expression at constant grain size and stress is given by

$$Q_c = -\frac{R \, d \ln D}{d \, (1/T)} + \frac{5R \, d \ln E}{d \, (1/T)}$$

or

$$Q_c = Q_{sd} - 5R \frac{T^2}{E} \left(\frac{dE}{dT}\right) \; . \qquad (15)$$

Thus, unless the modulus of elasticity does not vary with temperature Q_c will not be equal to Q_{sd}. In general, E does vary with temperature, al-though at moderately low temperatures the value associated with $5R \frac{T^2}{E} \frac{dE}{dT}$ is small ($\ll 2000$ cal/mole). However, if there is a strong temperature de-pendence of the elastic modulus, such as associated with the loss of ferro-magnetism in α-iron[4], then Q_c will differ very markedly from Q_{sd}. It should also be noted that equation (15) always predicts $Q_c > Q_{sd}$ as long as the modulus decreases with increasing temperature.

The magnitude of the difference between Q_c and Q_{sd} is dependent on the way in which the temperature dependent terms in $f(\sigma, T)$ enter the creep rate equation. Creep equations other than that given by equation (14) have been developed which contain different functions of the temperature in the

pre-exponential term. Three of the better known formulas are those

developed by Weertman and Nabarro, given as follows for constant L and σ :

Weertman (1955 dislocation climb model)[5] $\dot{\epsilon}_s$ = (const) $\dfrac{DE^{-3}}{T}$ (16a)

Weertman (1957 dislocation climb model)[27] $\dot{\epsilon}_s$ = (const) $\dfrac{DE^{-3.5}}{T}$ (16b)

Nabarro (1957 diffusional creep model)[38] $\dot{\epsilon}_s$ = (const) $\dfrac{D}{T}$. (16c)

Apparent activation energies for creep can be obtained by applying equa-

tion (13) to these relationships.

Cadmium was chosen as an example to evaluate the inequality of

Q_c to Q_{sd}, because the available evidence[16] indicated that the elastic

modulus of cadmium is a very strong function of temperature. Tests were

therefore conducted to determine the temperature dependence of the elastic

modulus of pure cadmium from room temperature up to the melting tempera-

ture. Parallel tests were also performed to determine the apparent acti-

vation energy for creep and to compare these data with the activation

energies predicted by equations (14), (16a), (16b) and (16c).

The average elastic modulus of polycrystalline cadmium (99.9 + %

pure) was determined in the temperature range from 273 to 588° K by meas-

uring the resonant frequency of rectangular specimens during transverse

free-free vibration. All tests were conducted in a helium atmosphere at

a pressure of about 1000 microns of Hg and the neutral frequency of vibra-

tion at room temperature was 790 cps. The modulus specimens had an aver-

age grain size of 1.5 - 2 mm, which was about the same size as the mini-

mum specimen dimension (the specimen dimensions in mm were 1.75 x 8.13

x 79.60). Complete details of the design of equipment and of the method

of measuring the resonant frequency have been given previously[2].

The curve of $E/E_{273^\circ K}$ versus temperature for cadmium is shown in Fig. 10. Included for comparison are the data of Koster[16] who determined the modulus in a similar manner at approximately the same frequency range. The purity and grain size of Koster's material were not reported. In the present investigation it was found that by driving the specimen at its second harmonic the E/E_{273} curve is displaced to higher temperatures, indicating that the steep drop in modulus with temperature, which begins at about 400° K, is due to a relaxation effect. Both curves were reproducible on heating and cooling. The magnitude of the relaxation is large and is most probably due to grain boundary relaxation. With this in mind, the difference between Koster's curve and the one obtained in this investigation may be due to a grain size difference.

In order to estimate the unrelaxed modulus at temperatures above the relaxation the low temperature unrelaxed modulus was extrapolated approximately parallel to the portion of the experimental curve where the relaxation appears completed (see Fig. 10). The small curvature in this extrapolation is reasonable in light of similar trends seen in other metals (see Fig. 6, for example). From the extrapolated portion of the curve the quantity $\frac{T^2}{E} \frac{dE}{dT}$ was calculated and applied to the creep formulas represented by equations (14) and (16a, b, c). The activation energies for creep predicted by these equations, appropriately corrected for all their temperature dependent terms, are shown in Fig. 11.

In order to investigate the actual dependence of Q_c with temperature, the creep behavior of pure polycrystalline cadmium (99.9999% pure) was studied from 325 to 550° K. Creep testing was done in compression
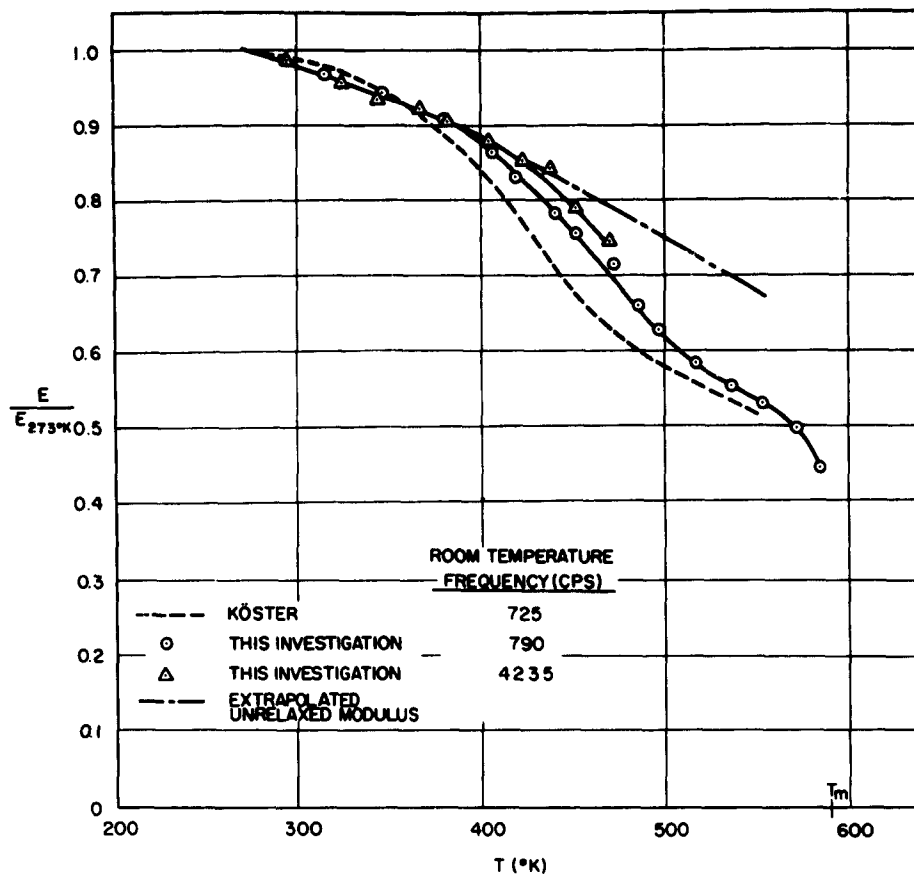
FIG. 10 Dynamic modulus of elasticity of polycrystalline cadmium as a function of temperature showing assumed unrelaxed modulus used for activation energy calculations.
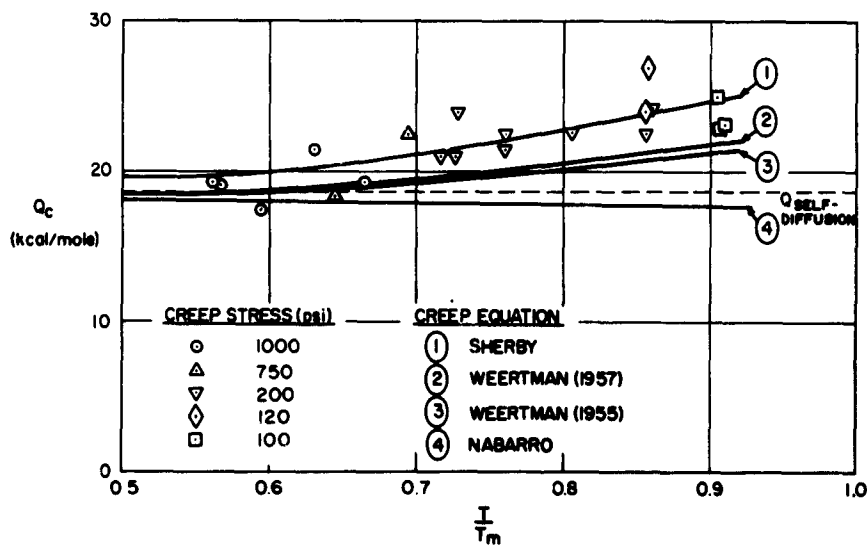

FIG. 11 The activation energy for creep of cadmium as a function of temperature according to various creep equations. Experimental values from the present investigation are included for comparison with theory.

using apparatus similar to that described previously[39] and temperatures were maintained constant to 1° C using hydrocarbon oil baths up to 200° C and a salt mixture of 60% KNO_3 - 40% $NaNO_2$ above 200° C. All creep specimens were cylindrical in shape with a length of 3/8" and diameter of 1/4 - 3/8". An annealing treatment of 1 hour at 310° C was given to all samples prior to testing and the resulting grain size was approximately 1-2 mm.

Apparent activation energies for creep were determined by the ΔT method[39] and a typical creep rate versus creep strain curve used for the determination of Q_c is shown in Fig. 12. Recrystallization often occurred after only a few percent of creep because of the extremely high purity of the material tested. For this reason the majority of tests were concluded after only two or three temperature changes. Q_c was not found to vary with either stress or strain. The experimentally determined values of Q_c are plotted in Fig. 11 as a function of temperature. All points are plotted at the mean temperature between the two test temperatures.

It is obvious from the data plotted in Fig. 11 that the apparent activation energy for creep of pure cadmium increases with test temperature. These results are consistent with those reported by Duran[40] where Q_c increased from a value of 20.0 kcal/mole at temperatures of 0.5 T_m to a value of 30.0 kcal/mole at temperatures above 0.8 T_m. This increase can be best explained by the temperature dependence of the elastic modulus and its influence on the calculation of Q_c. The relationship presented by equation (14) predicts the temperature dependence of Q_c well within the limits of experimental scatter (see Fig. 11), while the two creep equations derived by Weertman tend to underestimate the increase of Q_c. The
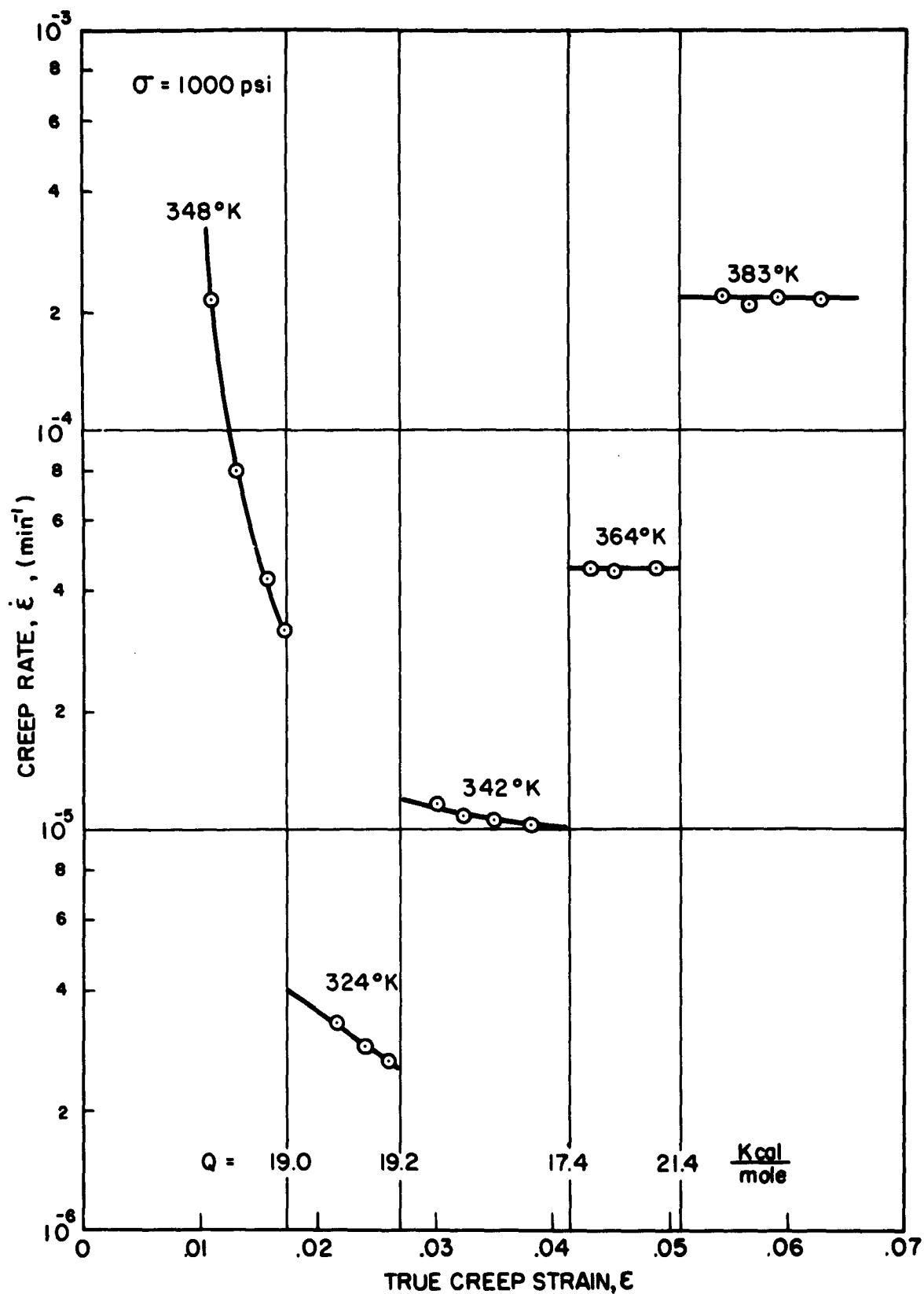
FIG. 12   Typical curves of log (creep rate) vs. true strain, ϵ, used in determining activation energies for creep of polycrystalline cadmium.

The diffusional creep model (which should apply only at very high temperatures and low stresses) actually predicts a slight decrease in Q_c with increasing temperature.

Analysis of equation (14) yields a technique useful in the direct calculation of _true_ creep activation energies. If tests at different temperatures are run at a constant σ/E ratio rather than just at a constant stress then the activation energy calculated from an Arrhenius type plot will be equal to the self-diffusion activation energy. This effect is illustrated in Fig. 13 where the steady state creep rate data of Servi and Grant[41] for high purity aluminum is plotted both for the case of constant σ and constant σ/E (the modulus of aluminum was taken from data of Fine[42]). For constant σ it is seen that Q_c increases with increasing test temperature and only approaches the value of Q_{sd} at test temperatures near $0.5 \, T_m$. The data plotted at constant σ/E, however, yield a temperature independent creep activation energy of 33 ± 1 kcal/mole which is very near to Q_{sd} ($Q_{sd} = 34 \, \frac{kcal}{mole}$ [43]).

The above analyses suggest a way of precisely correlating steady state creep rate data at various temperatures. In the past, it has been common to plot such data by means of the Zener-Hollomon parameter[44], namely

$$\sigma = f \, (\dot{\epsilon} e^{Q_c/RT}) \, . \tag{17}$$

This parameter has been shown to closely predict the behavior of many pure metals at elevated temperature, where the activation energy for creep is usually taken as that for volume self-diffusion[45]. However, since Q_c is not a constant but varies with temperature the Zener-Hollomon relation
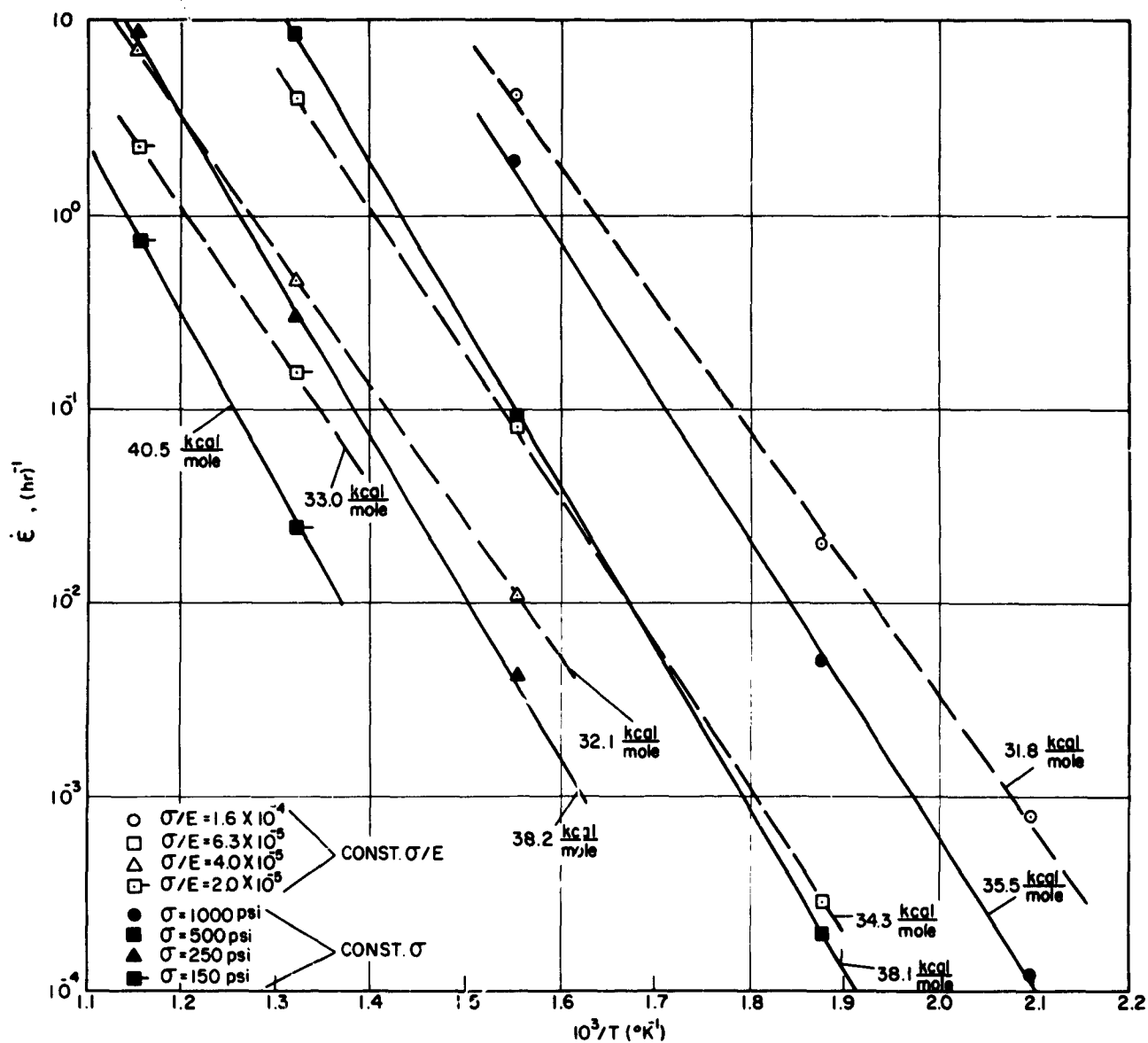
Fig.13 Activation energies for creep of aluminum as determined by plotting log $\dot{\varepsilon}$ vs. $1/T$ for constant σ and constant σ/E. Note constant values of Q_c obtained on the latter basis. Creep data after Servi and Grant[41], modulus data after Fine[42].

is not absolutely correct. Rather, the analyses presented in this investigation indicate that equation (17) should be modified by compensating the stress with a modulus term as follows

$$\frac{\sigma}{E} = f(\dot{\epsilon} \, e^{Q_c/RT}) \; . \tag{18a}$$

In this case Q_c will equal Q_{sd}. Since the diffusion coefficient D is given by $D_o e^{-Q_{sd}/RT}$, equation (18a) can be rewritten as

$$\frac{\sigma}{E} = f(\frac{\dot{\epsilon}}{D}) . \tag{18b}$$

The importance of the temperature dependence of the elastic modulus in the correlation of creep data by means of equation (18b) is seen in Fig. (14) where Servi and Grant's data is plotted as $\frac{\dot{\epsilon}s}{D}$ versus both $\frac{\sigma}{E}$ and σ. Although both plots fit the data well, the excellent correlation of the experimental points in the σ/E plot at high test temperatures (where the modulus correction is most important) once again illustrates the importance of taking into account the temperature dependence of E.

It is worth noting that if σ and 1/E have the same exponent, n, in a creep equation, as they do in equation (14), a plot of ln $\dot{\epsilon}$ vs. 1/T at constant σ/E yields a true activation energy for creep regardless of the value of this exponent. An alternative procedure consists of evaluating the quantity $d(\ln E^{-n})/d(1/T)$ which is equal to Q_c by equation (14). This procedure requires knowledge of the value of n which can only be obtained by conducting a series of creep tests at different stresses. Even though n is usually about 5 for pure metals, it generally is smaller for alloys. Thus, if activation energies are desired, especially in materials where n is unknown, plotting ln$\dot{\epsilon}$ vs. 1/T at constant σ/E to find Q_c has obvious advantages.
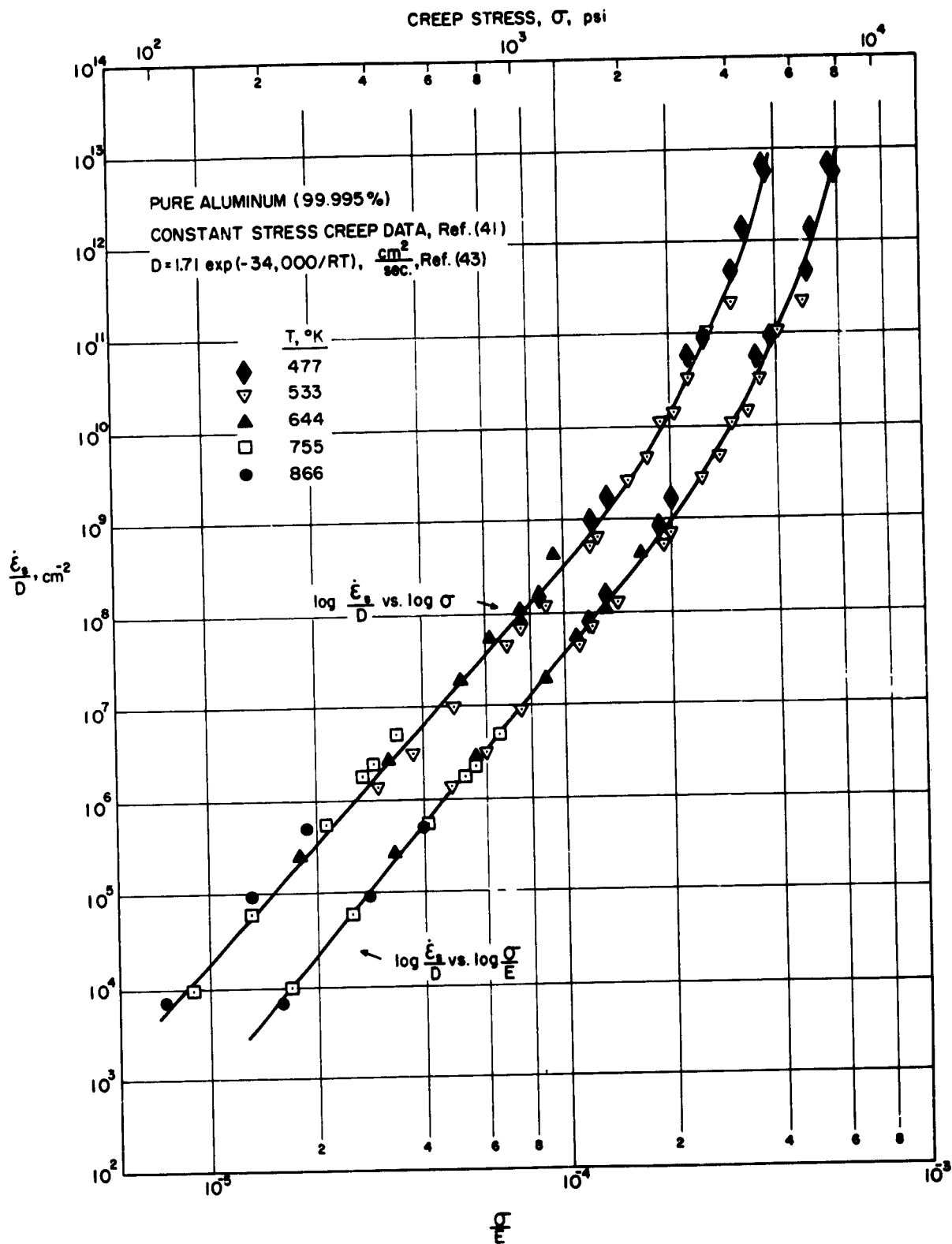
Fig. 14 Diffusion-compensated steady-state creep rate
($\dot{\epsilon}_s$/D) as a function of σ/E.   Plot of $\dot{\epsilon}_s$/D vs. σ
is shown for comparison.

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